



**UNIVERSITI PUTRA MALAYSIA**

**OXIDATION OF REACTIVE ORANGE 16 BY COPPER OXIDE  
SYSTEM**

**WONG WAN YUAN**

**FS 2006 41**

# **OXIDATION OF REACTIVE ORANGE 16 BY COPPER OXIDE SYSTEM**

**By**

**WONG WAN YUAN**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfilment of the Requirement for the Degree of Master of Science**

**July 2006**



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment  
of the requirements for the degree of Master of Science

## **OXIDATION OF REACTIVE ORANGE 16 BY COPPER OXIDE SYSTEM**

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**July 2006**

**Chairman: Associate Professor Abdul Halim Abdullah, PhD**

**Faculty: Science**

A commercial activated carbon (KI7080) sample was treated by  $\text{HNO}_3$  and followed by heat treatment at 500 and 700°C under a flow of  $\text{N}_2$ . Three types of copper oxide supported-activated carbon catalysts were prepared using impregnation techniques. 5 wt % of Cu was loaded for each catalyst and calcined at 500°C. Samples were characterized by FTIR, XRD and nitrogen adsorption isotherm studies. The adsorption-desorption isotherms of all samples showed a typical Type I with hysteresis loops of  $\text{H}_4$ .

The decolourisation of reactive orange 16 (RO16) by different advanced oxidation processes was investigated. The rate of colour removal was studied by measuring the absorbance at characteristic wavelengths. The effect of CuO dose,  $\text{H}_2\text{O}_2$  dose, UV light, added AC and catalyst was studied. These parameters influenced the decolourisation rate. The comparison between powdered and granular CuO was also studied. It was found that the decolourisation rate increased until an optimum  $\text{H}_2\text{O}_2$  dosage (60 ml of 1 M  $\text{H}_2\text{O}_2$ ), beyond which the reagent exerted an inhibitory effect.

For CuO/H<sub>2</sub>O<sub>2</sub> system, contribution of the leached Cu<sup>2+</sup> to the total colour removal by CuO/H<sub>2</sub>O<sub>2</sub> can be estimated approximately 40 %. The colour removal by CuO/H<sub>2</sub>O<sub>2</sub> system is an adsorption/oxidation process. The effect of UV on the decolourisation of RO16 was in the following order: CuO/UV/H<sub>2</sub>O<sub>2</sub> > CuO/H<sub>2</sub>O<sub>2</sub> > CuO/UV = CuO > UV/H<sub>2</sub>O<sub>2</sub> > H<sub>2</sub>O<sub>2</sub> > UV.

A simple kinetic model confirmed a pseudo-second order reaction for CuO, CuO/H<sub>2</sub>O<sub>2</sub>, CuO/UV/H<sub>2</sub>O<sub>2</sub>, CuO/UV, UV/H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, AC/CuO/H<sub>2</sub>O<sub>2</sub>, 5%Cu-ACN, 5%Cu-ACN/UV/H<sub>2</sub>O<sub>2</sub>, 5%Cu-ACN/H<sub>2</sub>O<sub>2</sub> and 5%Cu-ACN/UV systems.

The AC/CuO/H<sub>2</sub>O<sub>2</sub> system exhibited a lower efficiency compared to CuO/H<sub>2</sub>O<sub>2</sub> most probably due to decomposition of H<sub>2</sub>O<sub>2</sub> and reduction of Cu<sup>2+</sup>. The decolourisation efficiency of 5% Cu-ACN catalyst under four different conditions was observed in the following order: 5%Cu-ACN/UV/H<sub>2</sub>O<sub>2</sub> > 5%Cu-ACN/H<sub>2</sub>O<sub>2</sub> > 5%Cu-ACN/UV = 5%Cu-ACN. 5%Cu-ACN/UV/H<sub>2</sub>O<sub>2</sub> system was found to be the most efficient method on decolourisation of RO16 in this study.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
sebagai memenuhi keperluan untuk ijazah Master Sains

**PENGOKSIDAAN REAKTIF OREN 16 MENGGUNAKAN SISTEM KUPRUM  
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Oleh

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**Pengerusi: Profesor Madya Abdul Halim Abdullah, PhD**

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Satu karbon teraktif komersil (KI7080) telah dirawat dengan  $\text{HNO}_3$  dan diikuti rawatan haba pada 500 dan 700°C di bawah aliran  $\text{N}_2$ . Tiga mangkin kuprum oksida tersokong pada karbon teraktif telah disediakan dengan menggunakan teknik impregnasi. 5 wt% Cu dimuatkan ke dalam setiap mangkin and dikalsin pada 500°C. Sampel dicirikan dengan FTIR, XRD and isoterma penjerapan nitrogen. Isoterma penjerapan-penyahjerapan bagi semua sampel menunjukkan jenis I dengan lekuk histeresis  $\text{H}_4$ .

Pelunturan wana bagi reaktif oren 16 dengan proses pengoksidaan yang berbeza telah dikaji. Kadar penyingkiran warna dikaji dengan menyukat serapan pada ciri panjang gelombang. Kesan dos CuO, dos  $\text{H}_2\text{O}_2$ , lampu UV, AC yang ditambah dan mangkin telah dikaji. Parameter ini mempengaruhi kadar pelunturan warna. Perbandingan telah dibuat antara serbuk dan ganul CuO. Takat optimum  $\text{H}_2\text{O}_2$  yang diperlukan telah dipeperiksa. Didapati kadar pelunturan warna meningkat sampai satu dos  $\text{H}_2\text{O}_2$  (60 ml

1 M  $\text{H}_2\text{O}_2$ ) yang optimum, melebihi dos ini boleh menyebabkan kesan rencatan. Bagi sistem  $\text{CuO}/\text{H}_2\text{O}_2$ , sumbangan  $\text{Cu}^{2+}$  ini kepada pelunturan warna  $\text{CuO}/\text{H}_2\text{O}_2$  boleh dijanggakan sebanyak 40%. Pelunturan warna dengan sistem  $\text{CuO}/\text{H}_2\text{O}_2$  ialah satu process penyerapan/pengoksidaan. Kesan UV ke atas pelunturan warna RO16 adalah dalam order berikut:  $\text{CuO}/\text{UV}/\text{H}_2\text{O}_2 > \text{CuO}/\text{H}_2\text{O}_2 > \text{CuO}/\text{UV} = \text{CuO} > \text{UV}/\text{H}_2\text{O}_2 > \text{H}_2\text{O}_2 > \text{UV}$ .

Satu model kinetik yang mudah telah memastikan tertib tindak balas pseudo-kedua bagi sistem  $\text{CuO}$ ,  $\text{CuO}/\text{H}_2\text{O}_2$ ,  $\text{CuO}/\text{UV}/\text{H}_2\text{O}_2$ ,  $\text{CuO}/\text{UV}$ ,  $\text{UV}/\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{AC}/\text{CuO}/\text{H}_2\text{O}_2$ , 5% $\text{Cu-ACN}$ , 5% $\text{Cu-ACN}/\text{UV}/\text{H}_2\text{O}_2$ , 5% $\text{Cu-ACN}/\text{H}_2\text{O}_2$  dan 5% $\text{Cu-ACN}/\text{UV}$ .

$\text{AC}/\text{CuO}/\text{H}_2\text{O}_2$  menunjukkan kecekapan yang lebih rendah berbanding dengan  $\text{CuO}/\text{H}_2\text{O}_2$ . Ini disebabkan oleh penguraian  $\text{H}_2\text{O}_2$  dan pengurangan  $\text{Cu}^{2+}$ . Kecekapan pelunturan warna bagi mangkin 5% $\text{Cu-ACN}$  di bawah 4 keadaan yang berbeza telah dipermerhatikan dalam order 5% $\text{Cu-ACN}/\text{UV}/\text{H}_2\text{O}_2 > 5\%\text{Cu-ACN}/\text{H}_2\text{O}_2 > 5\%\text{Cu-ACN}/\text{UV} = 5\%\text{Cu-ACN}$ . Didapati sistem 5% $\text{Cu-ACN}/\text{UV}/\text{H}_2\text{O}_2$  adalah kaedah yang paling efektif untuk pelunturan warna RO16 dalam kajian ini.

## **ACKNOWLEDGEMENTS**

First and foremost, I would like to take this opportunity to express my earnest appreciation to my project supervisor, Associate Professor Dr. Abdul Halim Abdullah for his inspiring guidance, patience, constructive criticisms and generous support, which enabled me to complete this study successfully. I also wish to extend my gratitude to my co-supervisor, Associate Professor Dr. Mohd Ismail Yaziz for his invaluable suggestions and unlimited support during my studies.

My sincere gratitude also goes to my friends, lab mates, housemates and all the laboratory assistants and staffs of the Chemistry Department in UPM, particularly Acer, Salina, Li Yin, Sook Keng, Kong Hui, Wooi Long, Chuan Sheng, Mdm Choo, Mdm Rosrani and Ms Roraina.

Last but not least, grateful thanks are certainly due to my beloved family for their understanding attitude, spiritual support, continuous help and encouragement throughout my life.



I certify that an Examination Committee has met on 4<sup>th</sup> July 2006 to conduct the final examination of Wong Wan Yuan on her Master of Science thesis entitled “Oxidation of Reactive Orange 16 by Copper Oxide System” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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## **DECLARATION**

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



**WONG WAN YUAN**

Date: 10 JUL 2006

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## LIST OF ABBREVIATIONS

AC	Activated carbon
AC/HCl	Hydrochloric acid treated activated carbon
ACN	Nitric acid treated activated carbon
AOPs	Advanced Oxidation Processes
BDDT	Brunauer, Denning, Deming, Teller
BET	Brunauer-Emmett-Teller
$C_0$	Initial concentration of the reactant
$C_s$	Concentration of the solvent
5%Cu-ACN	5 wt% Cu catalyst supported on nitric acid treated activated carbon
Cu20/AC	20 wt% Cu catalyst supported on activated carbon
Cu20/AC-HF	20 wt% Cu catalyst supported on hydrofluoric acid treated activated carbon
Cu20/AC-HNO <sub>3</sub>	20 wt% Cu catalyst supported on nitric acid treated activated carbon
CuO	Copper Oxide
CuO-MAC	Modified activated carbon supported copper oxide catalyst
FT-IR	Fourier Transform Infra Red
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometer
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee of Powder Diffraction Standard



$K$	Adsorption coefficient of the reactant
$k_2$	Pseudo-second order rate constant
$k_{app}$	Pseudo-first order rate constant
$K_r$	Reaction rate constant
$K_s$	Adsorption coefficient of the solvent
MSW	Municipal solid waste
OAC	Non-treated activated carbon
$OH\cdot$	Hydroxyl radical
$OH_2\cdot$	Perhydroxyl radical
$q_e$	Amount of soluted sorbate sorbed at equilibrium concentration of the solvent
$q_t$	Amount of soluted sorbate on the surface of the sorbent at any time $t$
$R^2$	Correlation coefficient
RO16	Reactive Orange 16
$TiO_2$	Titanium Dioxide
TOC	Total Organic Carbon
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
UV	Ultraviolet
$V$	Oxidation potential
XRD	X-Ray Diffraction
$\theta$	Fraction of the surface covered by the reactant

## **CHAPTER 1**

### **INTRODUCTION**

Currently, it is estimated that industries dump 300 to 500 million tons of heavy metals, solvents, toxic sludge and other wastes into water sources annually. Water usage in the industrial sector is expected to increase from 752 cubic kilometers a year to 1,170 cubic kilometers a year by 2025 (Bender, 2004).

The textile dyeing and printing industries are among the several industries responsible for pollution of aquatic ecosystems. Over 700,000 tons of approximately 10,000 different types of dyes and pigments are produced annually worldwide. Nearly 50 % of these dyes are azo-type dyes. About 20 % of dye of the total world production is assumed to be discharged in industrial effluents during the textile dyeing process (Azbar *et al.*, 2004). Up to 50 % of reactive dyes, 8-20 % of disperse dyes and 1 % of pigments may be lost directly into effluents during the dyeing process (McMullan *et al.*, 2001).

Removal of color in wastewater generated by the textile industries is a current issue of discussion and regulation all over the world. Among the reactive dyes, the textile azo dyes have attracted the most attention with regard to its high environmental impact due to their widespread use, their potential to form toxic aromatic products and their low removal rate during primary and secondary treatment.

A variety of physical and chemical treatment methods are presently available for these dyes. Nevertheless these methods merely transfer the dye to a solid phase which requires further treatment (Carneiro *et al.*, 2004).

Biological processes such as sequenced anaerobic or aerobic digestion, have been proposed in the treatment of textile wastewater, but they are limited due to the fact that many of the dyes are not enobiotic and non-biodegradable (Behnajady *et al.*, 2004)

During the last two decades advanced oxidation processes (AOPs) that are combinations of powerful oxidizing agents (catalytic initiators) with UV or near-UV light have been applied for the removal of refractory organic pollutants and xenobiotics. Destructive oxidation of dyes and textile effluents have recently received considerable attention since coloured aromatic compounds have proven to be degraded effectively by a variety of homogeneous and heterogeneous AOPs . AOPs such as Fenton and photo-Fenton catalytic reactions,  $H_2O_2$ / UV processes and  $TiO_2$  mediated photocatalysis have been studied. A broad range of experimental conditions was established in order to reduce the colour and organic load of dye containing effluent wastewater.

The aim of this work was to evaluate the possibility of treatment alternative for reactive orange 16 (RO16) dye wastewater by copper oxide system. Since copper nitrate is the best catalyst in the catalytic oxidation of dyeing and printing wastewater, copper will be chosen as the active element to be deposited onto the porous support.

## **1.1 Study Objectives**

The objectives of this study are:

1. To study the decolourisation of reactive orange 16 (RO16) by CuO/H<sub>2</sub>O<sub>2</sub> system by varying the mass of CuO and concentration of H<sub>2</sub>O<sub>2</sub>.
2. To prepare and characterize copper oxide-modified activated carbon catalysts (CuO-MAC).
3. To examine the colour removal efficiency of RO16 by modified activated carbon (MAC) and CuO-MAC catalysts via adsorption.
4. To examine the colour removal efficiency of RO16 by a combination of CuO-MAC catalyst and H<sub>2</sub>O<sub>2</sub> with and without UV light via oxidation.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Oxidation**

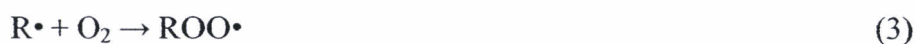
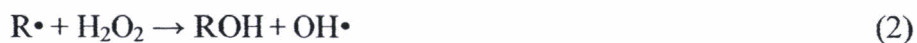
Oxidation is defined as a process of the electron loss from an atom or ion and also the combination of oxygen with other substances. The reactant that gains electrons is called the oxidation agent. The oxidizing agent contains the element that is being reduced (gains electron). If a substance gains electrons easily, it is said to be a strong oxidizing agent.

##### **2.1.1 Advanced oxidation process (AOPs)**

AOPs have common principles in terms of the participation of hydroxyl radicals that are assumed to be operative during the reaction. Although it is claimed that there are other species involved, the active species responsible for the destruction of contaminants in most cases seems to be the  $\text{OH}^\bullet$  which is unstable and quite reactive. Due to the instability of the  $\text{OH}^\bullet$  radical, it must be generated continuously “in situ” through chemical or photochemical reactions (Oliver *et al.*, 2000).

Hydroxyl radicals may attack organic molecules by abstracting a hydrogen atom from the molecule (Clarke and Knowles, 1982). A common pathway for the degradation of organics by the  $\text{OH}^\bullet$  is described as follows:





A wide variety of advanced oxidation processes are available:

- chemical oxidation processes using  $\text{H}_2\text{O}_2$ , ozone, combined ozone & peroxide, hypochlorite, Fenton's reagent etc.
- ultra-violet enhanced oxidation such as UV/ozone, UV/ $\text{H}_2\text{O}_2$ , UV/air
- wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant)

AOPs ( $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) for the degradation of non-biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods. AOPs based on the generation of very reactive and oxidizing free radicals have been used with increasing interest due to their high oxidizing power. Production of these radicals is achieved either using single oxidants or combinations of ozone,  $\text{H}_2\text{O}_2$  and UV radiation (Glaze and Kang, 1989) and also, with the combination of  $\text{H}_2\text{O}_2$  with ferrous ions in the so-called Fenton's reagent (Walling, 1975). The oxidation using Fenton's reagent has proven to be a promising and attractive treatment method for the effective decolourisation and degradation of dyes. Complete degradation of organic compounds by Fenton's reagent include phenols, various chlorinated phenols, aromatics like benzene, toluene, xylene,